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COMPLETE SPECIFICATION

NO DRAWINGS

Sandable thermoplastic organic Solder composition

We, E.I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

The invention is concerned with a moldable organic composition and more particularly is directed to a sandable thermoplastic organic solder composition suitable for filling recessed areas and depressions in metal structures such as automobile bodies.

It is conventional in the manufacture and repair of automobiles to fill unsightly recessed areas and depressions with lead solders. These areas occur particularly where sheet metal surfaces are joined by riveting, welding or the like and it is necessary, in order to provide a smooth surface suitable for painting, that imperfections, dents and crevices be filled with a composition which will adhere tenaciously and can thereafter be sanded smooth. Lead solders which have been used for many years in this application are deficient in a number of important respects. Apart from toxicity problems associated with lead solders, a substantial amount of skill is necessary in their application so that trained personnel are essential to their use. There is a manifest need for a solder material free from the toxicity of lead compounds and which can be applied by relatively unskilled labor to provide a smooth high quality product. Obviously a composition which would fulfill these requirements and at the same time exhibit additional improvements over lead solders would be a substantial contribution to the art.

In accordance with this invention there is provided a sandable solder composition suitable for joining and filling depressions and recesses in solid articles. This composition consists essentially of:

an intimate mixture of

(1) 60-80% by volume of a thermoplastic organic polymer of a monomer mixture consisting essentially of (a) 10-95% by weight of one or more ethylenically unsaturated fluorocarbon monomers, at least 20% of monomers (a) being tetrafluoroethylene and (b) 90-5% by weight of one or more ethylenically unsaturated monomers, at least 83% of monomers (b) being a monoethylenically unsaturated hydrocarbon monomer having less than nine carbon atoms, said polymer having the following characteristics: flow rate, as hereinafter defined, less than 100 at 295°C/2160 g., decomposition temperature at least about 300°C, a second order transition temperature less than about 45°C; and

(2) 20-40% by volume of inorganic particulate solids.

The organic solder composition of this invention overcomes the principal deficiencies of lead solders and also obviates the main problems which have attended organic materials heretofore offered for use as substitutes therefor. The instant compositions are particularly useful in that they can be applied in relatively thick layers without the high degree of skill required in using lead solders. Thus only one or two applications are necessary when a relatively deep cavity requires filling. The composition of this invention is capable of providing thin or thick coatings as desired with a single pass (as by flame-spraying) and repeated passes are usually unnecessary. Unlike prior art or-

ganic compositions used for hiding imperfections in metal articles, the compositions of this invention provide exceptionally good wet adhesion to metals, particularly to iron or steel substrates.

The thermoplastic organic polymers used in this invention are polymers of a monoethylenically unsaturated fluorocarbon monomer or a mixture of such monomers and at least one other monoethylenically unsaturated hydrocarbon. A preferred fluorocarbon monomer is tetrafluoroethylene (TFE) and this monomer is preferably used as the sole fluorocarbon monomer in the compositions of this invention, although it can be used as a mixture with other monoethylenically unsaturated fluorocarbon monomers, so long as TFE is present in an amount of at least 20% by weight. The higher the content of TFE in such mixtures, the better is the quality of the solder composition. Specific examples of such fluorocarbon monomers are vinylidene fluoride (VF_2), hexafluoropropene (HFP), chlorotrifluoroethylene (CTFE) and dichlorodifluoroethylene (DCDFE). Preferred compounds in this group because of the ease of copolymerization are perfluoro olefins containing 2 or 3 carbon atoms. Preferred fluorocarbon mixtures are TFE/VF_2, TFE/CTFE/VF_2, TFE/HFP/VF_2 containing at least 50% TFE by weight because next to compositions of this invention containing TFE as the sole fluorocarbon, these mixtures produce the highest quality organic solders.

The thermoplastic organic polymer of this invention is a copolymer of at least two monomers, the first being a fluorocarbon monomer above described and a second essential monomer being a monoethylenically unsaturated hydrocarbon copolymerizable with the fluorocarbon monomer by conventional addition polymerization techniques. Thus the thermoplastic polymer of this invention is a polymer of a monomer mixture "consisting essentially of" tetrafluoroethylene and said hydrocarbon monomer and the expression "consisting essentially of" is intended to have its accepted meaning as requiring the named ingredients to be present but not excluding unnamed materials which do not detract substantially from the properties of the composition. Preferred hydrocarbon monomers are those containing less than 9 carbon atoms particularly from 2-4 carbon atoms. Suitable example include ethylene (E), propylene (Pr), butylene (B), isobutylene (IB), pentene, hexene, neohexene and their homologs.

Optionally the thermoplastic polymer used in this invention can obtain other monomeric units in addition to the two essential monomeric units described above and without detracting from the properties thereof. Thus the polymer can be a terpolymer of the fluorocarbon monomer, an olefin and an "acidic monomer" which is preferably an α,β-unsaturated acid or lower alkyl (less than nine carbon atoms) ester thereof. More specifically, this polymerizable monomer is defined as:

(1) An unsaturated aliphatic carboxylic acid of at most ten carbon atoms wherein the unsaturation is monoethylenic and which can contain up to one substituent selected from chlorine, bromine or carboxyl; i.e., a polymerizable monomer of the formula RCOOH where R is alkenyl which can contain up to one chlorine, bromine or carboxyl substituent and which contains at most nine carbon atoms. Preferably the acid is unsubstituted.

(2) An unsaturated alicyclic hydrocarboncarboxylic acid of at most ten carbon atoms wherein the unsaturation is monoethylenic; i.e., a polymerizable monomer of the formula R′COOH where R′ is alicyclic and is preferably alkenylcycloalkyl.

(3) Tertiary lower alkyl esters of groups (1) and (2) wherein the total carbon content is at most ten carbon atoms; i.e., polymerizable monomers of the formulas RCOOR″ and R′COOR″ where R″ is tertiary lower alkyl and the entire compound contans at most ten carbon atoms.

(4) A cyclic anhydride formed by two carboxyl groups of an unsaturated hydrocarbondicarboxylic acid of at most ten carbon atoms wherein the unsaturation is monoethylenic; i.e., a polymerizable compound of the formula $R'''(CO)_2O$ wherein R‴ is alkenylene of at most eight carbon atoms.

Representative of the polymerizable acidic monomers described above are acrylic acid (AA), methacrylic acid (MAA), α-chloroacrylic acid, α-bromoacrylic acid, itaconic acid, t-butyl acrylate and 3-methylenecyclobutanecarboxylic acids which can be prepared as described in U.S. 2,914,541.

Because they can be copolymerized by economical processes to given polymers having desirable properties, the lower alkenoic acids and 3-methylenecyclobutanecarboxylic acids are especially preferred. The C_3-C_4 acrylic acid, i.e. acrylic acid and methactylic acid, are the most preferred acid monomers, because of a combination of availability, ease of copolymerization and good properties of the resulting copolymers.

Copolymers of this invention (which term refers to polymers prepared from at least two monomers) containing less than about 7% combined acidic monomer (based on total polymer weight) usually have relatively superior properties, particularly melt stability in molten form, and therefore con-

stitute a preferred class. In general, the properties conferred on the copolymers by the presence of the combined acidic monomer are not markedly increased by having more than about 4% combined acidic monomer, and polymers containing up to about 4% combined acidic monomer therefore form an especially preferred class of products. The best properties of terpolymers of this invention are realized with relatively small proportions of combined acidic monomer (e.g., as low as about 0.01%). The preferred lower limit is about 0.1%.

Mixtures of two or more fluorocarbon monomers, two or more olefins and two or more acidic monomers can be used in the copolymerization process, and can, correspondingly, be present in the combined state in the polymers, but polymers of this invention prepared from more than three monomers do not usually exhibit advantages over terpolymers. Generally these polymers contain 10 to 95% by weight fluoroinated monomer units with the remainder being hydrocarbon monomer or a mixture of hydrocarbon and acidic monomer units. Preferably these polymers contain 30 to 60% fluoroinated monomer on this basis. However, the terpolymers described above containing an acidic monomer are more universally useful than those without and can be applied to substrates by hot melt bulk application methods as well as by flame-spraying to produce smooth sandable surfaces having excellent adhesion. Compositions of this invention containing two-component polymers are applied by flame-spraying techniques.

The polymers of the invention are made by conventional methods well known to those skilled in the art. In one convenient method, the monomers to be polymerized and an initiator, usually in the presence of an inert liquid medium, are heated in a closed container under moderate superatmospheric pressures, e.g., about 300-2500 psi (pounds per square inch) (ca. 20-170 atmospheres); the pressure being created and maintained by injecting water into the system. For some monomer systems, particularly those involving acidic monomers, it is advantageous to use water-free liquids as reaction media and for repressuring.

Conventional free-radical initiators, such as peroxides, azonitriles and metal and ammonium persulfates, can be used as initiators. Organic-soluble initiators (i.e., initiators soluble in typical organic solvents) are preferred, particularly organic peroxides such as benzoyl peroxide; *tert*-butyl peroxypivalate, and *tert*-butyl peroxide. The temperature will of course be determined largely by the particular initiator used. Water, lower alkanols, and lower carboxamides such as dimethylacetamide, together with mixtures thereof, can be used as inert media. Lower alkanols, e.g., ethyl alcohol, isopropyl alcohol, and *tert*-butyl alcohol, are particularly suitable, especially when mixed with water. Inert organic media, while more costly than water, have the advantage that copolymers prepared in their presence show less tendency to appear as hard lumps in the product mixture and are correspondingly easier to work up. When a liquid medium other than pure water is used, its composition of course will change during the process as more water is injected to create and maintain the desired pressure.

Thermoplastic polymers useful in this invention have a "flow rate" of less than about 100 at 295°C./2160 g. which means that flow rate is measured for purposes of this invention at 295° with a weight of 2160 grams. The method of ASTM 1238-62T is used. Flow rate can be defined as the weight of molten polymer in grams that passes through a standard orifice in ten minutes at a given temperature and under a given extrusion weight.

Similarly, softening temperatures, determined as "sticking temperatures" (which directly reflects molecular weight, at least in part) as low as 60°C. and as high as 230°C. can be utilized. For the reasons given above, a preferred class of copolymers are those having sticking temperatures between about 90°C. and 180°C. "Sticking temperature" can be defined as the lowest temperature of a heated brass block at which a solid polymer leaves a molten trail when moved across the block in contact with the block. A softening temperature lower than 100°C. below the decomposition temperature of the polymer is essential when the organic solder composition is to be applied by flame-spraying. Such a low softening point is not essential for hot melt bulk mass applications or other mechanical means of application but does provide an added safety factor by way of improved melt stability.

The polymers used in this invention are also characterized by a decomposition temperature greater than about 300°C. This means that at 300°C the polymers will suffer a weight loss of no more than 5% over a period of two hours. These polymers also have a Second Order Transition Temperature (t_g) of less than 45°C. and preferably less than 10°C. Polymers having a t_g higher than this can be used if their effective t_g is lowered to this range as by addition of a suitable plasticizer such as a dialkyl phthalate (i.e. dioctylphthalate; dimethyl phthalate, dibutyl phthalate, dicyclohexyl phthalate, the phthalate of dimethyl cellosalve, etc.) or a silicone fluid or chlorinated biphenyl, etc.

It is essential that the organic solder compositions of this invention contain 20 to 40% by volume of inorganic particulate solids.

These particulate solids can be prepared from a metal or an inert inorganic compound such as a silicate (e.)., magnesium silicate) which is stable at elevated temperatures. Normally the compositions of the instant invention will be applied to a substrate in the form of a melt or partial melt and it is important that the chemical composition remain substantially unchanged under the application conditions as well as during any subsequent baking or heating.

When the composition of this invention is to be applied to a substrate by flame-spraying techniques, it must be in the form of solid particles having a size of −48+200 mesh, that is, the particles should pass through a No. 50 and be retained on a No. 200 U.S. Standard Sieve (1940 series). While a small proportion of particles larger than 48 mesh and smaller than 200 mesh may be present, desirably all of the particles will fall within this range even when the composition is to be applied by hot melt bulk mass techniques although not really necessary in the latter case.

Any of the inorganic pigments commonly used in paints and plastics can be used as the particulate solids in the composition of this invention so long as they have the above characteristics with respect to particle size and stability. The particulate solids can be metallic powders such as those of aluminum or the like, copper, iron, steel and bronze, or inorganic non-metallic particles, but preferably at least 50% of the particulate solids utilized in this invention will be metallic because with such a composition the organic solders of this invention are not only easily sanded to provide smooth surfaced products but exhibit a metallic sheen which greatly improves the appearance of the soldered area. Aluminum powder is particularly prefered for use in this invention along with an equal quantity by volume of magnesium silicate. Maximum economy is achieved by use of inexpensive non-metallic powders such as magnesium silicate, aluminum silicate, hydrous calcium sulphate, barium sulphate, silicon dioxide, potassium aluminum silicate, calcium carbonate, calcium silicate, titanium dioxide, zinc oxide, zinc sulphide/zinc sulphate, antimony oxide, iron pyrophosphate, carbon, iron oxide, cuprous oxide, sulpho silicate of alumina and soda and ferric ferrocyanide.

The compositions of this invention can be conveniently prepared by first dissolving the thermoplastic polymer in a suitable solvent, such as xylene, which is inert with respect to the compounds of the composition. Heating and agitation are usually utilized to expedite dissolution. The particulate solids are then added to the solution with stirring in order to produce a good dispersion. The amount of solvent should be chosen so that simply cooling the resulting mixture will provide a finely divided precipitate which upon separation from the liquid present and drying will be of a particle size suitable for use in flame-spraying or by knife application as a solder. Alternatively the solid particulate mixture can be recovered by spray drying techniques.

If the particulate solids mixture obtained by this procedure contains a large proportion of excessively large particles the mixture can be sifted through a No. 50 sieve or the large particles can be comminuted by any convenient means. In any event the ultimate mixture should be as uniform and homogeneous as possible for easy handling and best results.

The invention is illustrated by the following specific examples.

Example 1

700 Grams of xylene was heated to 125°C. in a resin pot fitted with a stirrer and reflux condenser. 50 Grams of tetrafluoroethylene/isobutylene/acrylic acid terpolymer (67/33/0.04, flow rate 1.5 at 295°C./2160 g., decomposition is less than 5% at 300°C. for two hours; t_g=40°C.) was added to the hot xylene. This mixture was stirred until a clear solution formed. 28 Grams of magnesium silicate and 28 grams of atomized aluminum were added and stirring was continued for an additional 15 minutes. The heat source was removed and the dispersion was allowed to cool with stirring until a precipitate formed (at about 75°C.). The cooled mixture was poured into excess acetone and a finely divided precipitate filtered on felt and air dried. The powder was sifted through a 50 mesh screen. Free films pressed from this powder at 260°C. and 5000 psi had a tensile strength of 2100 psi and an elongation at break of 3.5%.

The powdered material described above was flame-sprayed onto a lap joint panel using an acetylene-air mixture in a Schori Process Model P Gun. Excess polymeric solder was removed from the surface by sanding to give a smooth surfaced panel with the welded lap seam completely undectable through the solder. Sections cut from the filled joint had tensile strengths of 1600 psi and elongations of 1%.

Example 2

The powdered material described in Example 1 was flame-sprayed as in Example 1 except that when the joint was filled the supply of powder to the gun was stopped and a cool stream of air was directed to the surface of the polymer to harden the surface. The mass of polymer was then compacted using a "Bantum Bully Air Hammer" until the surface developed a smooth, nonporous glaze. Sections cut from this filled joint had tensile strengths of 4800 psi and elongations of 3.4%.

Example 3

500 Grams of a TFE/IB polymer (1:1 molar ratio, flow rate=8.3 at 295°C./2160 g., t_g=41°C., softening point=190°C., decomposition at 300°C. is less than 5% in two hours) was sifted through a 50 mesh screen and placed in a one gallon glass jar. 410 Grams of calcium carbonate were added to the jar. The two powders were mixed thoroughly by agitating the jar for 15 minutes.

Some of the resulting powder mixture was flame-sprayed using a Schori Process Model P Gun with an acetylene/air flame at 220-260°C. There was considerable overspray of fine powder during the spraying operation. The overspray contained a high concentration of filler. Another portion of the mixture was pressed into a film at 260°C. for 30 seconds at 10,000 psi. The film had a tensile strength of 5,300 psi and an elongation at break of 4%.

Example 4

Samples of the powder mixture described in Example 3 were passed successively through an impact pin mill to grind the polymer and disperse the calcium carbonate filler. The resulting powder flowed more freely and 100% of the material passed through a 100 mesh screen.

A portion of this screened powder was flame-sprayed by a Schori Process Model P Gun with an acetylene/air flame at 240-260°C. A second portion of the screened powder was pressed from the mixture at 260°C. for 30 seconds at 10,000 psi. The resulting film had a tensile strength of 3,400 psi and an elongation at break of 3.0%.

Example 5

2,500 Ml. of xylene was heated in a seven liter stainless steel beaker to 125°C. with a three-inch propeller blade stirrer immersed in the liquid. 500 Grams of the TFE/IB polymer described in Example 3 was added to the hot xylene. The mixture was stirred at 125°C. until a clear viscous solution was obtained. 400 Grams of calcium carbonate was added to the hot solution and stirring was continued for five minutes at 125°C. before the heat source was removed. The dispersion was then allowed to cool slowly with stirring until the temperature reached 75°C. Stirring was stopped and the dispersion cooled to room temperature. Following dilution of the dispersion with acetone (5,000 ml.) and agitation to break up the particles, the solids were filtered onto a felt filter pad and washed with fresh acetone and air dried. The dried precititate was sifted through a 50 mesh screen to get uniform sized particles.

A portion of the dried powder described above was flame-sprayed using a Schori Process Model P Gun with an acetylene/air flame at 240-260°C. Another portion of the powder was pressed into a film in a Carver Press at 260°C. and 10,000 psi for 30 seconds. The films had a tensile strength of 3,100 and an elongation of 3.6%.

Samples of the powder described above were applied to an auto body steel panel with a depression 2 inches in diameter and 1/8 inch deep. The panel was first solvent wiped with chloroform to remove any oil and then preheated with a flame to 260°C. The polymer was flame-sprayed into the depression using enough excess so that the depression was completely filled after the panel was subsequently pressed at 15 psi pressure in a Carver Press at 260° to compact the material. The soldered panel was allowed to cool to room temperature and then sanded using a power belt sander with 60 grit aluminum oxide open grain paper. The surface was finished with 100 grit "Adolox" open grain paper to give a smooth surface. The panels were subsequently spray painted with a commercial pigmented lacquer to produce a coated panel with the original depression no longer visible.

Example 6

A portion of the hot (125°C.) dispersion described in Example 5 was passed through a steam jacketed sand-grinder to achieve a more uniform dispersion of the calcium carbonate in the polymer solution. After the effluent from the sand-grinder cooled to room temperature the polymer precipitated and the resulting mixture was diluted with 5,000 ml. of acetone and agitated to break up the particles. The precipitate was filtered through a felt filter and washed with more acetone to remove residual xylene. The powder was air dried and sifted through a 50 mesh screen.

A portion of the powder thus prepared was flame-sprayed using a Schori Process Model P Gun with an acetylene/air flame at 240-260°C. Another portion was pressed into film at 260°C. and 10,000 psi for 30 seconds. The films had a tensile strength of 3,400 psi and an elongation of 7.0%. This material flame-sprayed exceptionally well with little overspray and good coalescence.

An auto body steel panel with a 1/8 inch deep and 2 inch diameter depression was solvent wiped with chloroform to remove any oil from the surface. A portion of the powder described above was then placed in the depression and the whole panel was placed in a Carver Press. After the panel reached 260°C. the powder was compacted into the depression by applying 15 psi pressure with the press, and the filled panel was allowed to cool to room temperature. Excess solder was removed using a power belt sander with 60 grit paper and the surface was finished with 100 grit paper. When the smooth panel was spray painted with a commercial pigmented lacquer the filled depres-

sion was no longer visible.

Example 7

205 Grams of the TFE/IB polymer described in Example 3 was placed on a two-roll mil at 220°F. with 25 mils clearance between rolls. The polymer was rolled until a clear stock was formed. 168 Grams of calcium carbonate was slowly added to the mill stock and the resulting mixture was milled for an additional ten minutes. A mixture was thus obtained which was uniform in appearance and became hard and brittle on cooling.

Films pressed from this mill stock at 260°C. at 10,000 psi for 30 seconds had a tensile strength of 2,400 psi and an elongation of 3.0%.

An auto body steel panel with a 1/8 inch deep by 2 inch diameter depression was solvent wiped with chloroform to remove any surface oil. Several layers of 25 mil film of the mill stock were laid over the surface of the depression. The polymer and panel were then heated to 260°C. in an oven and pressed under 15 psi pressure in a Carver Press to cause the solder to flow into the depression. After cooling to room temperature the excess solder was removed by sanding with a power belt sander with 60 grit paper and finished with 100 grit paper. Subsequent painting of the panel with a conventional commercial pigmented lacquer rendered the filled depression no longer visible; the panel was of course first coated with primer and sealer.

Example 8

Thin films of TFE/IB, TFE/IB/AA, TFE/IB/Pr, TFE/IB/Pr/AA, TFE/E/Pr, TFE/E/Pr, TFE/IB/E, TFE/IB/E/AA and TFE/IB/VF_2/AA prepared as in the above examples, were applied to solvent wiped auto body steel panels by either flame-spraying or melt pressing in the Carver Press or by both techniques as indicated in Table I.

As controls, similar thin films of several commercial resins customarily used to coat steel substrates and also known to provide acceptable adhesion were compared with the above panels for wet adhesion. These included a polyamide resin, a polyester resin copolymer of ethylene glycol/terephthalate acid/isophthalic acid, a polycarbonate resin of bisphenol A and phosgene, and a diglycidyl ester resin of bisphenol A/ethylene diamine/dicarboxylic fatty acid.

All panels were cut with a cross-hatch pattern to determine their initial resistance to delamination. Attempts were made, using a sharp knife, to peel the coatings off the steel panels starting with a corner at the center of the cross hatch. This test rates the delamination strength (adhesion of the coating) as follows:

Adhesion	*Length of Peeled Coating*
Excellent	None
Good	<1/16 inch
Fair	1/16-1/8 inch
Poor	>1/8 inch

All panels were rated excellent initially but they were then submerged in boiling water at reflux for 300 hours, removed, dried and allowed to reach room temperature. Adhesion was again checked by the knife peel test with the following results:

TABLE I

Polymer	*Adhesion when applied by flame-spraying*	*Adhesion when applied as bulk hot melt*
TFE/IB (64/36)	Good	Good
TFE/IB/AA (63/35/2)	Excellent	Good
TFE/IB/Pr (64/30/6)	Good	Fair
TFE/IB/Pr/AA (63/18/14/5)	Excellent	Good
TFE/E/Pr (77/21/2)		Fair
TFE/IB/E (73/18/9)	Good	Fair
TFE/IB/E/AA (52/37/11/0.8)		Excellent
TFE/IB/VF_2/AA (52/32/16/0.8)	Good	Fair
Polyamide resin	Poor	Poor
Polyester resin	Fair	Fair
Polycarbonate resin	Poor	Fair
Diglycidyl ester resin	Poor	Poor

WHAT WE CLAIM IS:—

1. A sandable solder composition suitable for filling depressions in solid articles and consisting essentially of an intimate mixture of

(1) 60-80% by volume of a thermoplastic organic polymer of a monomer mixture consisting essentially of (a) 10-95% by weight of one or more ethylenically unsaturated fluorocarbon monomers, at least 20% of monomers (a) being tetrafluoroethylene and (b) 90-5% by weight of one or more ethylenically unsaturated monomers, at least 83% of monomers (b) being a monoethylenically unsaturated hydrocarbon monomer having less than nine carbon atoms, said polymer having the following characteristics: flow rate as hereinbefore defined, less than 100 at 295°C/2160 g., decomposition temperature at least about 300°C, second order transition temperature less than about 45°C, and

(2) 20-40% by volume of inorganic particulate solids.

2. A composition according to claim 1 in the form of a −48+200 U.S. standard mesh solids mixture, said polymer having a softening temperature, as hereinbefore defined, which is at least 100°C below the decomposition temperature of the polymer.

3. A composition according to claim 1 or 2, in which the particulate solids are a mixture of metal particles and inorganic non-metallic particles, the mixture containing at least 50% metal particles.

4. A composition according to claim 1 or 2, in which the particulate solids are inorganic non-metallic particles.

5. A composition according to any of claims 1 to 4, in which component (a) of said polymer consists of tetrafluoroethylene alone.

6. A composition according to any of claims 1 to 5, in which the hydrocarbon monomer is a C_2-C_4 hydrocarbon.

7. A composition according to any of claims 1 to 6, in which the hydrocarbon monomer is isobutylene.

8. A composition according to any of claims 1 to 7, in which the thermoplastic organic polymer contains, as monomer units, 30-60% tetrafluoroethylene and 70-40% ethylenically unsaturated hydrocarbon by weight.

9. A composition according to any of claims 1 to 7, in which the polymer also contains, in an amount up to 7% based on polymer weight, polymerized units of a monoethylenically unsaturated compound which is (1) an aliphatic carboxylic acid containing less than 10 carbon atoms which may, if desired, contain chlorine, bromine or carboxy substituents, or (2) an alicyclic carboxylic acid containing less than 10 carbon atoms which may, if desired, contain chlorine, bromine or carboxy substituents, or (3) a tertiary lower alkyl ester of classes (1) or (2).

10. A composition according to claim 9, in which the polymer contains polymerized units of a C_3-C_4 acrylic acid.

11. A sandable solder composition according to claim 1 substantially as herein described in any of the Examples.

12. A metal substrate having a depression filled with a composition as claimed in any of claims 1 to 11.

13. A metal substrate according to claim 12 painted with a synthetic polymeric coating composition.

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